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(54) Soluble Denatured Whey Protein

(57) A method of preparing soluble denatured whey protein compositions, comprises raising the pH of an aqueous solution of native whey protein to a value of more than 6.5 and then heating the solution at a temperature and/or for a time greater than that which causes denaturing of the whey protein. The soluble denatured whey protein compositions obtained may be in the form of solutions, concentrates or dry powders and are suitable for incorporation in foodstuffs.

Two Dutch Applications
79.08455 filed Nov 79
77.05936 probably filed 1977

SPECIFICATION

A Method for the Preparation of Modified Whey Proteins

The invention relates to a method for the preparation of modified whey proteins which modification may for example be carried out by thermal treatment.

Heating whey proteins in cheese whey or casein whey will generally lead to insoluble denatured complexes having poor functional properties, such as foaming, emulsification or gelation which properties are related to the solubility of the protein.

It is known in general that upon heating a maximum amount of protein precipitates at a pH -value of about 4.6.

Jelen and Schmidt (Can. Inst. of Food Sci. and Technol. J. *9* (1976) 2, 61—65) have attempted to redissolve the insoluble complexes obtained by this known heating of a cheese whey by heating the same again. For that purpose the protein had to be adjusted to a pH-value above 11.0 at 75°C. Heating these proteins at such high pH-values is generally conducive to the formation of bad tasting products and may lead to the formation of toxic compounds.

Modler and Emmons (J. Dairy Science *60* (1977) 2, 177—184) have attempted to prevent the bad taste when modifying whey proteins by heating the whey at about 90°C at a pH-value between 2.5—3.5. The protein denatured during this heating may be separated from the whey by adjusting the solution to a pH-value of 4.6 at which the protein becomes (reversibly) insoluble. The precipitate may then be separated from the whey by centrifuging.

This method has the drawback that it requires large quantities of acid and base, respectively, to adjust the whey to the required pH-value, whereas the productivity of this method is low. Moreover the thus obtained protein does not have improved functional properties, compared with the not heated protein.

Furthermore from the Dutch Patent Application 77. 05936 it is known to heat suspensions of protein-containing material to a temperature of from 70 to 100°C, to subsequently adjust the pH-value of 6.6—8.0 by means of certain basic substances and to dry the suspension after being heated to said temperature for 1—120 minutes.

Although the application relates mainly to the treatment of mono-cellular proteins, such as yeast, whey protein suspensions may be used as well. A well tasting product is obtained which may be used as a substitute for solid egg constituents and skimmed milk powder when baking bread.

The thus heated suspensions are only suitable for use in those cases where the solubility and the functional properties associated therewith are not essential.

Finally it is known from the French Patent Specification 1,555,757 to heat whey at a pH-value of 6.2—6.4 at 90—100°C for some time and then to adjust to a pH-value of 4.6 while maintaining the said temperature. When the precipitation is completed the precipitated protein is separated by cooling and centrifuging. A protein suspension is obtained based on a permanently insoluble protein and lacking the functional properties associated with a good solubility.

It has now been found that when adjusting the pH-value of solutions of native whey protein to a pH-value above 6.5 and subsequently heating the solution at a temperature-time combination surpassing that causing the whey protein to denature, there will be obtained a solution of soluble denatured whey protein the functional properties of which, such as overrun and foam stability are maintained whereas surprisingly there are also obtained special structure properties.

Furthermore it has been found that upon cooling this protein may be separated in a relatively high yield at a pH-value of about 4.6. From the DSC-thermogram it appears than an irreversible denaturization has occurred.

The invention therefore relates to a method of preparing soluble denatured whey protein compositions by heating solutions of native whey protein and is characterized by adjusting the solution to a pH-value above 6.5 and subsequently heating the adjusted solution at a temperature-time combination surpassing that causing the whey protein to denature and optionally neutralizing, concentrating and/or drying the product obtained upon cooling.

It is of importance therein to cool the solution, preferably to a temperature below 30°C before adjusting the pH-value. When adjusting the pH-value without a preceding cooling the solubility of the obtained protein is much lower.

The pH-value at which the heating is performed should be at least a pH-value of 6.5. The upper limit of the applicable pH-region is not critical. As higher pH-values are conducive to the formation of undesired compounds and may likewise detrimentally affect the taste, the pH-value is preferably adjusted to 6.5 to 8.0 and in particular to 7.0—7.5. It is preferred that the pH-value for neutralization is about 6.5.

The time-temperature combination for denaturing the protein is related to the composition of the protein and of the medium in which this protein is present and may easily be determined by means of devices suitable for that purpose such as by means of a differential thermo-analysis. The period of time during which the heating is performed is dependent on the heating temperature. It is preferred to utilize a period of time of more than 1 minute and a temperature above 75°C and in particular a temperature of 80—90°C for 15—30 minutes.

Although it is obvious to use solutions the protein concentration of which amounts to about 0.5% by weight, like in whey, it is also possible to operate at higher percentages if so desired. For many applications of the protein solutions prepared in accordance with the invention it may be advantageous to start from a solution in which the protein content and the lactose content approximate those of milk. It is then preferred to utilize a protein concentration region of 2.0—4.0% by weight. At percentages above 5% by weight there is the risk of gelation of the protein.

It has been found that better functional properties such as emulsifying and gelating properties are obtained when starting from a previously desalted whey for instance by means of ion exchange (see example IV).

It has been found that the whey protein is subject to such a change in structure that without the presence of casein to which the yogurt structure is considered to be partially accountable, a good yogurt may be prepared.

The protein compositions obtained in accordance with the invention are sensitive to multivalent kations. The addition of for instance 20 mg Ca^{++}/g protein to a whey protein solution of 5% by weight of protein heated previously in accordance with the invention at a pH-value of 7.5 at 85°C for 20 minutes (solution A) thus imparts improved structure properties whereby a thickening effect in liquid products for example may be achieved. The products according to the invention distinguish in this respect from corresponding products which have not been heated (solution B) or have been heated at a pH-value between 2.5 and 3.5 (solution C) (vide table A). This effect is enhanced by renewed heating. The appropriate salts are preferably added after emulsification whereby structure may be imparted to whipped fat-containing products.

Table A
Viscosity in mPa.s Determined at the Temperature Indicated

	Solution A		*Solution B*		*Solution C*	
Temperature (°C)	*without Ca^{++}*	*with Ca^{++}*	*without Ca^{++}*	*with Ca^{++}*	*without Ca^{++}*	*with Ca^{++}*
20	2.5	11	2	2	2	2.5
30	2.5	12	2	2	2	2.5
40	2.5	13	2	2	2	3.5
50	2.5	12	2	2	2	4
60	2.5	17	2	2	2	6
70	2.5	60	2	2	3.5	11

A similar structure imparting effect like obtained upon addition of for instance Ca^{++} may also be achieved by a slow acidification to a pH-value of about 5.6 or below. The addition of 0.2% of gluconic acid-δ-lactone to a whey protein solution previously heated in accordance with the invention at 5% by weight of protein and a pH-value of 7.5 at 85°C for 20 minutes (solution D) thus led to a continuously further increasing viscosity at room temperature whereby the formation of a firm gel structure occurred. When contrary thereto the lactone was added to a whey protein solution not previously heated in accordance with the invention (solution E) there was obtained a watery solution at 5% by weight of protein containing a light precipitate (vide table B).

Table B

	Solution D		*Solution E*	
Period of time for acidification (min)	*viscosity (mPa.s)*	*pH*	*viscosity (mPa.s)*	*pH*
70	2.8	5.77	2.8	5.80
80	3.5	5.75	2.8	5.78
90	5.0	5.70	2.8	5.73
100	19.0	5.66	2.8	5.68
110	54.0	5.65	2.8	5.65

For the recovery of the soluble denatured whey proteins from the whey there may utilized the aforesaid property that these proteins have a maximum insolubility at a pH-value of about 4.6.

From the solutions obtained in accordance with the method of the invention concentrates or dry products are prepared by cooling the solution if required neutralizing the same preferably at a pH-value

of about 6.5 and then concentrating and/or drying said solution. Likewise after completion of the heating and the cooling the pH-value may be reduced to a pH-value of about 4.6, followed by centrifugation, whereupon the sediment is dissolved at a pH-value of about 6.5 and the solution thus obtained is concentrated and/or dried. The dry composition will then have a relatively higher protein content than in case the drying is carried out directly.

Advantageously the solution may be subjected to ultrafiltration whereupon the retentate is concentrated and/or dried. It has been found that thereby a higher flux is achieved than in case of compositions which have not been heated.

By way of example a Gouda cheese whey was desalted by means of a Lewatite ion exchanger till a desalting degree of 90%. The desalted whey having a protein content of 0.7% was adjusted to a pH-value of 7.5 and thereupon heated to 85°C for 20 minutes. After cooling to 20°C the pH-value was reduced to a pH-value of 6.5. The solution thus obtained was subjected to ultrafiltration with the aid of tubelike membranes at a temperature of 13°C, a pressure of 0.2 mPa and a flow rate of 95 l/min. The retentate was concentrated by evaporation at reduced pressure and finally dried. The obtained powder was used in the preparation of food stuffs such as salad dressing and artificial yogurt.

Table C

Reduction in volume (%)	*flux (l/m²/h)*	
	before heating	*after heating*
2	50	60
5	45	64
10	42	62
20	40	57.5
30	39	56
40	37.7	55
50	36	54
60	35	52
70	34	48
80	32	40
90	20	28

The invention also relates to the preparation of food-stuffs while employing whey protein compositions obtained in accordance with the invention in which use is made of the structure properties or the functional properties of the obtained soluble denatured whey protein.

Example I

Cheese whey having a protein content of 0.7% was heated at a pH-value of 6.75 at 80°C for 20 minutes. After cooling the whey to room temperature the pH-value of the whey was lowered to a pH-value of 4.6. By centrifuging at 1000×g for 10 minutes there could be separated 50% of the nitrogen containing material originally present in the whey.

The isolate thus obtained contained 92% denatured protein soluble at a pH-value of 6.7.

Example II

For the preparation of a salad dressing there was prepared a 35% milk fat emulsion by homogenizing 700 g milk fat in 1300 g of a 2.2% whey protein solution. To this emulsion there were added:

5 to 6% of whey protein powder (60% protein)
3% of mustard
1.5% of NaCl
4% of sugar
1 drop of spice oil/100 g emulsion
6 ml of table vinegar/100 g emulsion

After completion of the preparation the emulsion was stored in the refrigerator for 16 hours whereupon the firmness was determined penetrometrically by means of a SUR-penetrometer and a circular 10 g disc (diameter of 70 mm) having cylindrical perforations (fall time 50 sec.). The dressing has the same properties as a salad dressing made when using egg yolk. When using not heated native whey protein compositions the salad dressing remained in watery condition.

Example III

For preparing an aritifical yogurt there was prepared a 35% fat emulsion like in example II which emulsion was diluted with a solution of 3.8% whey protein in skimmed milk permeate to form a 3% fat

emulsion. Thereupon 6 g NaH_2PO_4/l was incorporated in this emulsion which emulsion was then pasteurized at 65°C for 30 minutes. Thereupon the emulsion was inoculated with 0.05% ISt.+0.05% RR lacto bacillus (=yogurt culture) and cultured at 32°C for 16 hours. If the whey protein heated in accordance with the invention was used the following result was obtained: viscosity determined by means of a Posthumus funnel=33 sec (at 20°C). pH=4.3 and acidity=114°N. The acetaldehyde content was 13 mg/kg. If a native whey protein solution was used the emulsion was subject to flocculation upon acidification.

Example IV

An aliquot of pasteurized Gouda cheese whey was desalted with the aid of a Lewatite ion exchanger to a desalting degree of 90%. The desalted whey was then concentrated at 30°C by reverse osmosis till a protein concentration of 3% was obtained. An other aliquot of the starting whey was not desalted but concentrated directly at 30°C by means of a film evaporator till a protein concentration of 3% was obtained.

Each of the two compositions was divided into three portions; the first set was not heated, the second set was heated at a pH-value of 6.0 at 85°C for 20 minutes and the third set was heated at a pH-value of 7.5 at 85°C for 10 minutes. The six obtained solutions were further concentrated by ultrafiltration. Some functional properties of the products prepared in these manners were determined in accordance with the methods described in Neth. Milk Dairy J. 29 (1975) 198 and indicated in the following table.

Table D

	not heated		*heated at pH=6.0*		*heated at pH=7.5*	
	desalted	*not desalted*	*desalted*	*not desalted*	*desalted*	*not desalted*
solubility (NSI at pH=6.5)	98.7%	94.8%	69.3%	43.6%	97.9%	73.8%
light transmission (0.15% of protein)	80.7%	78.9%	16.5%	11.0%	79.5%	46.2%
overrun (10% of protein)	1800%	1200%	530%	170%	1540%	950%
foam stability (10% of protein)	70%	60%	100%	0%	100%	100%
emulsifying action (0.15% of protein, 4% of fat)	49.5%	36.9%	27.7%	5.0%	41.8%	3.5%

Claims

1. A method of preparing soluble denatured whey protein compositions, which comprises raising the pH of an aqueous solution of native whey protein to a value of more than 6.5 and then heating the solution at a temperature and/or for a time greater than that which causes denaturing of the whey protein.

2. A method according to claim 1, in which, following the heating step, the solution is cooled and then neutralised and concentrated and/or dried.

3. A method according to claim 1 or 2, in which the pH of the solution is adjusted to 6.5 to 8.0.

4. A method according to any of claims 1 to 3, in which the pH of the solution is adjusted to 7.0 to 7.5.

5. A method according to any of claims 1 to 4, in which the solution is heated at a temperature above 75°C for more than 1 minute.

6. A method according to claim 5, in which heating is effected at 80—90°C for 15 to 30 minutes.

7. A method according to any of claims 1 to 6, in which the initial whey protein solution has a dry solids content of less then 15% by weight and a protein content of less than 5% by weight.

8. A method according to claim 7, in which the initial whey protein solution has a protein content of 2.0 to 4.0% by weight.

9. A method according to any of claims 1 to 8, in which the initial solution contains desalted whey.

10. A method according to any of claims 1 to 9, in which, following the heating step, the solution is cooled, the pH is reduced to 4 to 5, the solution is then centrifuged, and the sediment obtained is dissolved in water at a pH of 6.5 to 7.0 and the resulting solution is concentrated and/or dried.

11. A method according to any of claims 1 to 9, in which, following the heating step, the solution is cooled and then subjected to ultrafiltration and the retentate is concentrated and/or dried.

12. A method of preparing soluble denatured whey protein compositions, substantially as herein described in any of the Examples.

13. Soluble denatured whey protein compositions in the form of solutions, concentrates or dry powders when prepared by the method claimed in any of the preceding claims.

14. Foodstuffs which contain a soluble denatured whey protein composition as claimed in claim 13.

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